TABLE 2 MW: TABLE 1 CAS: TABLE 2 RTECS: TABLE 2

METHOD: 1450, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 2

COMPOUNDS: (synonyms in Table 2)	n-amyl acetate	t-butyl acetate	isobutyl acetate	sec-amyl acetate
	2-ethoxyethyl acetate	methyl isoamyl acetate	n-butyl acetate	ethyl acrylate
	n-propyl acetate	sec-butyl acetate	isoamyl acetate	

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ OSHA PEL
-MAX: 10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 2X OSHA PEL [1] (10-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.05 to 0.09; see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE - INJECTION: 200 - 225 °C
- DETECTOR: 250 - 300 °C
- COLUMN: 60 to 100 °C (Table 1)

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: stainless steel, 3 m x 3-mm, 5% FFAP on 100/120 mesh Chromosorb WHP

CALIBRATION: solutions of compounds in CS_2

RANGE: Table 1

ESTIMATED LOD: 0.02 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.02 [1]

APPLICABILITY: This method can be used for simultaneous analysis of 2 or more substances by changing the gas chromatographic conditions (e.g., temperature programming). High humidity greatly reduces sampler capacity and breakthro ugh volume.

INTERFERENCES: None identified. Alternate columns (e.g., 10% SP-1000 on Chromosorb WHP) may be useful if interferences are encountered.

OTHER METHODS: This method combines and replaces Methods S31, S32, S35, S37, S41, S44 through S48, and S51 [3]. Method 1457 (Ethyl Acetate) gives a capillary column procedure which may be useful for the esters in this method.

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 0.1% (v/v) benzene or 1% (v/v) tridecane, dodecane, undecane or other suitable internal standard
2. Analyte, reagent grade
3. Helium, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
4. Refrigerant, bagged ("Blue Ice," or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1450-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-µL, readable to 0.1 µL, 25-, 50- and 100-µL.
7. Volumetric flasks, 10-mL
8. Pipet, volumetric, 1-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment with bagged refrigerant.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

   NOTE: The desorption efficiency of 2-ethoxyethyl acetate has been found to decrease with the resident time of the desorbed solution with charcoal [4]. After 30 min. desorption transfer the supernatant solution of 2-ethoxyethly acetate to a clean 2-mL vial and seal with a crimp cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.02 to 10 mg analyte per sample.

a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
b. Analyze together with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).

9. Determine desorption efficiency (DE) at least once for each lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1450-1. Inject sample aliquot with autosampler, or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The methods listed below were issued on December 6, 1974, except for S51, which was issued on January 17, 1975 [2]. Atmospheres of each compound were generated in dry air by calibrated syringe drive and 10-L air samples were taken [1]. Collection efficiency in humid air and sample stability were not tested. Spiked samplers were used to study measurement precision and desorption efficiency (DE). Results are as follows:

		Overall					Measurement		
Compound	Method [3]	Range, mg/m^3	Breakthrough[1] (<)	Bias %	$\hat{S}_{rT}$	Accuracy (± %)	Range, mg per sample	DE[2]	$\hat{S}_r$
n-amyl acetate	S51	208-871	34.2	0.3	0.051	10.3	2.6-10	0.87	0.019
sec-amyl acetate	S31	349-1460	20.9	-4.1	0.071	15.4	3.3-13	0.93	0.012
n-butyl acetate	S47	352-1475	20.5	0.3	0.069	10.4	3.5-14	0.94	0.020
sec-butyl acetate	S46	478-2005	16.5	-2.4	0.054	11.3	4.7-19	0.93	0.017
t-butyl acetate	S32	424-1780	14.3	-8.6	0.091	22.2	4.7-19	0.94	0.039
2-ethoxyethyl acetate	S41	262-1100	34.6	9.6	0.062	19.4	2.5-11	0.79	0.024
ethyl acrylate	S35	50-210	>45	-7.1	0.054	15.7	0.5-2	0.95	0.029
isoamyl acetate	S45	208-874	32.3	-7.1	0.056	15.6	2.6-10	0.91	0.010
isobutyl acetate	S44	306-1280	21.5	1.8	0.065	11.1	3.5-14	0.94	0.016
methyl isoamyl acetate	S37	143-601	>45	-2.6	0.058	11.6	1.5-6	0.93	0.021
n-propyl acetate	S48	384-1610	17.9	6.9	0.056	16.8	4.2-17	0.93	0.018

[1] 5% breakthrough, 0.2 L/min, at high end of concentration range in dry air.
[2] Averaged over mass range shown.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] User check, UBTL, NIOSH Sequence #4121-N (unpublished, November 15, 1983).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] Corelson, D., SRI, Menlo Park, CA., Personal communication with NIOSH (1988).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Table 1. Operational details.

Compound	M.W. mg/m3 = 1 ppm @ NTP MW mg/m^3 = 1 ppm		Working range mg/m^3 @ 10 L	Measurement Range, mg per sample	Column Temperature,°C
n-amyl acetate	130.18	5.32	50 to 1575	0.5 to 16	90
sec-amyl acetate	130.18	5.32	65 to 1950	0.65 to 20	95
n-butyl acetate	116.16	4.75	71 to 2130	0.7 to 21	90
sec-butyl acetate	116.16	4.75	95 to 2850	1 to 28	60
t-butyl acetate	116.16	4.75	95 to 2850	1 to 28	70
2-ethoxyethyl acetate	132.16	5.40	54 to 1620	0.5 to 16	100
ethyl acrylate	100.11	4.09	10 to 300	0.1 to 3	70
isoamyl acetate	130.18	5.32	50 to 1575	0.5 to 16	90
isobutyl acetate	116.16	4.75	70 to 2100	0.7 to 21	70
methyl isoamyl acetate	144.22	5.90	30 to 900	0.3 to 9	90
n-propyl acetate	102.13	4.18	84 to 2520	0.8 to 25	70

Table 2. General information

Compound, Formula, and RTECS	Synonyms	OSHA/NIOSH/ACGIH, ppm	BP, °C	IV @ 0 (mm Hg)
n-amyl acetate $CH_3COO(CH_2)_4CH_3$; $C_7H_{14}O_2$ AJ1925000	acetic acid 1-pentanol ester; CAS #628-63-7	TWA (STEL) 100/100/100	149	0.5(4)
sec-amyl acetate $CH_3COOCHCH_3(CH_2)_2CH_3$; $C_7H_{14}O_2$ AJ2100000	acetic acid 2-pentanol ester; CAS #626-38-0	125/125/125	134	0.9(7)
n-butyl acetate $CH_3COO(CH_2)_3CH_3$; $C_6H_{12}O_2$ AF7350000	acetic acid butyl ester; CAS #123-86-4	150/150(200)/150(200)	126	1.3(10)
sec-butyl acetate $CH_3COOCH(CH_3)CH_2CH_3$; $C_6H_{12}O_2$ AF7380000	acetic acid 1-methyl propyl ester; CAS #105-46-4	200/200/200	112	1.3(10)
t-butyl acetate $CH_3COOC(CH_3)_3$; $C_6H_{12}O_2$ AF7400000	acetic acid 1, 1-dimethylethyl ester; CAS #540-88-5	200/200/200	98	not available
2-ethoxyethyl acetate $CH_3COO(CH_2)_2OCH_2CH_3$; $C_6H_{12}O_3$ KK8225000	Cellosolve acetate; acetic acid ethylene glycol monoethyl ether ester; CAS 111-15-9	100[a]/0.5[a]/5[a]	156	0.3(2)
ethyl acrylate CH_2=$CHCOOCH_2CH_3$; $C_5H_8O_2$ AT0700000	2-propenoic acid ethyl ester; CAS #140-88-5	25[a]/4 LOQ[b]/5[ab] (15 ppm)	99	3.9(30)
isoamyl acetate $CH_3COO(CH_2)_2CH(CH_3)_2$; $C_7H_{14}O_2$ NS9800000	acetic acid 3-methyl-1-butanol ester; CAS #123-92-2	100/100/100	142	0.5(4)
isobutyl acetate $CH_3COOCH_2CH(CH_3)_2$; $C_6H_{12}O_2$ AI4025000	acetic acid isobutyl ester; CAS #110-19-0	150/150/150	117	1.7(13)
methyl isoamyl acetate $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$; $C_8H_{16}O_2$ SA7525000	acetic acid 4-methyl-2-pentanol ester; 1,3-dimethyl butyl acetate; "sec-hexyl acetate"; CAS #108-84-9	50/50/50	146	0.5(3.8)
n-propyl acetate $CH_3COO(CH_2)_2CH_3$: $C_5H_{10}O_2$ AJ3675000	acetic acid n-propyl ester; CAS #109-60-4	200/200 (250)/200 (250)	102	3.3(25)

[a] Skin
[b] Carcinogen